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Title: FUEL COMPOSITION CONTAINING DETERGENT COMBINATION
AND METHODS THEREOF

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BACKGROUND OF THE INVENTION

Field of the Invention

10 This invention involves a fuel composition that includes a combination of detergents and methods that utilize the fuel composition to operate and to control deposits in an internal combustion engine.

Description of the Related Art

15 Hydrocarbon fuels generally contain substances that tend to form deposits in the fuel delivery system of an internal combustion engine such as the fuel injectors in diesel engines and the intake valves in gasoline engines. These deposits, if allowed to build up, can significantly reduce engine performance in terms of power output, fuel economy and exhaust emissions. It is highly desirable to incorporate detergents into hydrocarbon fuels that are effective in controlling deposits by
20 inhibiting their formation and facilitating their removal so that engine performance is maintained or improved.

Graiff et al. in European Publication No. EP 534551A1 published on March 31, 1993 disclose a gasoline composition that comprises a gasoline and a mixture of
25 a) a polyamine selected from the group consisting of an aliphatic alkylene polyamine containing at least one olefinic polymer, a Mannich polyamine, and mixtures of the aliphatic alkylene polyamine and the Mannich polyamine and b) a hydrocarbyl poly(oxyalkylene) aminocarbamate.

Cunningham et al. in U.S. Patent No. 5,679,116 issued October 21, 1997 disclose fuel additive compositions comprising a) at least one detergent/dispersant
30 which is a derivative of a hydrocarbon-substituted dicarboxylic acid or anhydride, a hydrocarbon having a polyamine attached, and/or a Mannich condensation product, b) a cyclopentadienyl complex of a transition metal and c) a liquid carrier or additive induction aid.

Croudace et al. in International Publication No. WO 90/10051 published September 7, 1990 disclose a fuel composition comprising a gasoline and an additive combination comprising one or more C₆+ primary amines, one or more gasoline dispersants selected from the group consisting of polyalkylamines and
5 Mannich bases, and a fluidizer oil.

Daly in U.S. Patent No. 5,873,917 issued February 23, 1999 discloses a fuel composition comprising a gasoline, a polyether alcohol, a hydrocarbylphenol, and optionally a third component comprising a nitrogen-containing dispersant to include hydrocarbyl-substituted amines, Mannich dispersants, and polyetheramines.

10 Wright in U.S. Patent No. 5,169,410 issued December 8, 1992 discloses a method to stabilize gasoline mixtures comprising adding to the gasoline a combination of a phenylenediamine having at least one N-H group and a strongly basic organo-amine comprising a Mannich reaction product.

The present invention is directed to a fuel composition that includes a
15 combination of two nitrogen-containing detergents and that is unexpectedly much more effective and efficient in controlling deposits in a hydrocarbon fueled internal combustion engine compared to fuel compositions that include a combination of either nitrogen-containing detergent with a fluidizer.

20 SUMMARY OF THE INVENTION

It is an object of the present invention to control deposits in an internal combustion engine so that engine performance is maintained or improved.

An additional object of this invention is to control deposits in a gasoline engine.

25 Another object of this invention is to control deposits in a diesel engine.

The objects, advantages and embodiments of the present invention are in part described in the specification and in part are obvious from the specification or from the practice of this invention. Therefore, it is understood that the invention is claimed as described or obvious as falls within the scope of the appended claims.

30 To achieve the foregoing objects in accordance with the invention as described and claimed herein, a fuel composition of this invention useful for a spark or a compression ignition internal combustion engine comprises a hydrocarbon fuel,

a combination of nitrogen-containing detergents comprising a hydrocarbyl-substituted polyamine and a Mannich reaction product of an alkyl-substituted hydroxyaromatic compound with an aldehyde and a polyamine having at least one reactive N-H group, and optionally a fluidizer comprising a polyether, a polyetheramine, or mixtures thereof where the weight ratio of the hydrocarbyl-substituted polyamine to the Mannich reaction product is about 0.2:1 to 1:0.2, where each of the nitrogen-containing detergents is present at about 20-100 ppm by weight, and where the weight ratio of the fluidizer to the combination of nitrogen-containing detergents is less than 0.5

Another embodiment of this invention is a method of operating an internal combustion engine which comprises fueling the engine with the fuel composition of this invention where the hydrocarbon fuel is a gasoline or a diesel fuel, and where the gasoline or diesel fuel optionally contains an oxygenate comprising methanol, ethanol, methyl tert-butyl ether, ethyl tert-butyl ether, methyl tert-amyl ether, or mixtures thereof.

A further embodiment of this invention is a method of controlling deposits in an internal combustion engine which comprises fueling the engine with the fuel composition of this invention where the hydrocarbon fuel is a gasoline or a diesel fuel, and where the gasoline or diesel fuel optionally contains an oxygenate comprising methanol, ethanol, methyl tert-butyl ether, ethyl tert-butyl ether, methyl tert-amyl ether, or mixtures thereof.

DETAILED DESCRIPTION OF THE INVENTION

A fuel composition of the present invention useful for a spark or a compression ignition internal combustion engine comprises a hydrocarbon fuel; a combination of nitrogen-containing detergents comprising a hydrocarbyl-substituted polyamine and a Mannich reaction product of an alkyl-substituted hydroxyaromatic compound, an aldehyde and a polyamine having at least one reactive N-H group; and optionally a fluidizer comprising a polyether, a polyetheramine, or mixtures thereof where the weight ratio of the hydrocarbyl-substituted polyamine to the Mannich reaction product is about 0.2:1 to 1:0.2, each of the nitrogen-containing detergents is present

at about 20-100 ppm by weight, and the weight ratio of the fluidizer to the combination of nitrogen-containing detergents is less than 0.5

The hydrocarbon fuel of the present invention is well known to those skilled in the art. Hydrocarbon fuels are generally derived from petroleum by various refinery processes. The hydrocarbon fuel can be a gasoline or a diesel fuel. The gasoline or diesel fuel optionally can contain an oxygenate or oxygen-containing molecule up to a level of about 25% by weight of oxygenate. Oxygenates include alcohols, ethers, ketones, esters, nitroalkanes, or mixtures thereof. Commonly used oxygenates include methanol, ethanol, methyl tert-butyl ether, ethyl tert-butyl ether, methyl tert-amyl ether, or mixtures thereof. Gasoline, suitable for use in spark ignition engines, generally boils in the range from 30 to 230°C and has a research octane number typically in the range of about 90 to 100. Diesel fuel, suitable for use in compression ignition engines, generally boils in the range from 140 to 400°C and has a cetane number in the range from 25 to 60.

The hydrocarbyl-substituted polyamine of the present invention has a hydrocarbyl substituent with a number average molecular weight of about 500 to 5000, preferably about 700 to 2000, and more preferably about 900 to 1500. The hydrocarbyl substituent is a univalent radical of carbon atoms that is predominantly hydrocarbon in nature but can have nonhydrocarbon substituent groups to include hydroxy groups and can contain heteroatoms. The hydrocarbon substituent can be derived from a polyolefin having a number average molecular weight as described above for the hydrocarbyl substituent. The polyolefin can be a homopolymer derived from one olefin or a copolymer derived from two or more olefins. The olefin can have 2 to about 10 carbon atoms and includes ethylene, propylene, butene isomers, decene isomers, and mixtures of two or more thereof. The polyolefin includes polyethylenes, polypropylenes, polybutenes and copolymers of ethylene and propylene. A preferred polyolefin is a polyisobutylene prepared by polymerization of a refinery stream containing about 30 to 60% by weight isobutylene using a Lewis acid catalyst such as aluminum trichloride or boron trifluoride. The polyolefin can be a polyisobutylene having at least 70% of its olefin double bonds at a terminal position on the carbon chain as the highly reactive vinylidene isomer which is also described below for the Mannich reaction product.

The polyamine portion of the hydrocarbyl-substituted polyamine of the present invention is derived from a polyamine containing two or more amine nitrogen atoms and having at least one reactive N-H group. The polyamine can be aliphatic, cycloaliphatic, heterocyclic or aromatic and includes alkylenediamines, polyalkylenepolyamines, and hydroxy-containing polyamines. Polyamines that can be used in preparing the hydrocarbyl-substituted polyamine include ethylenediamine, 1,3-propylenediamine, N,N-di-methyl-1,3-propanediamine, N-aminoethylpiperazine, N-aminopropylmorpholine, N,N'-di-butyl-para-phenylenediamine, diethylenetriamine, triethylenetetramine, 2-(2-aminoethylamino)ethanol, and mixtures thereof. In another instance the hydrocarbyl-substituted polyamine is derived from the group consisting of ethylenediamine, diethylenetriamine, N,N-dimethyl-1,3-propanediamine, 2-(2-aminoethylamino)ethanol, and mixtures thereof.

The hydrocarbyl-substituted polyamine can be prepared from the polyolefin and the polyamine as detailed above by several methods as described in U.S. Patent 6,193,767 to include 1) halogenating a polyolefin followed by reaction with a polyamine, 2) hydroformulating a polyolefin followed by reaction with a polyamine and finally hydrogenation of the aldehyde-polyamine reaction intermediate, and 3) epoxidizing a polyolefin followed by reductive amination or amination with a polyamine to form a polyamine or hydroxy-containing polyamine derivative respectively. A preferred method of preparation involves chlorinating a polyisobutylene so that it contains at least one chlorine atom. The chlorinated polyisobutylene is then reacted with the polyamine generally at elevated temperatures of about 120°C or higher. A solvent can be used to facilitate the reaction. Excess polyamine can be used to avoid cross-linking to include dimer formation as well as aid in hydrogen chloride removal although an inorganic base such as sodium hydroxide or sodium carbonate is usually employed to remove the hydrogen chloride. U.S. Patent 5,407,453 describes the method of halogenating a polyolefin followed by reaction with a polyamine.

The Mannich reaction product of the present invention is derived from the reaction of an alkyl-substituted hydroxyaromatic compound, an aldehyde, and a polyamine having at least one reactive N-H group. The hydroxyaromatic portion of the alkyl-substituted hydroxyaromatic compound comprises phenol, ortho-cresol, or

mixtures thereof. The alkyl-substituent of the alkyl-substituted hydroxyaromatic compound can be derived from a polyolefin which can be a homopolymer, copolymer, or mixtures thereof. The polyolefin can have a number average molecular weight of about 200 to 5000, preferably about 300 to 3000, and more preferably about 400 to 1500. In one instance the polyolefin can have a number average molecular weight of about 400 to 700 and in another instance about 900 to 1500. These polyolefins can be prepared from olefin monomers of 2 to about 10 carbon atoms to include ethylene, propylene, isomers of butene, isomers of decene and mixtures of two or more thereof. The polyolefins include polyethylenes, polypropylenes, polybutenes and copolymers of ethylene and propylene. A preferred polyolefin is a polyisobutylene derived from a refinery stream having an isobutylene content of about 30 to 60% by weight. A more preferred polyolefin is a polyisobutylene having at least 70% of its olefinic double bonds at a terminal position on the carbon chain as the vinylidene type. Highly reactive polyisobutylenes having a high vinylidene isomer content include Glissopal® marketed by BASF. The alkyl-substituted hydroxyaromatic compound can be prepared by well known methods including alkylating a hydroxyaromatic compound such as phenol with a polyolefin such as polyisobutylene using a Lewis acid catalyst like boron trifluoride.

The aldehyde used to prepare the Mannich reaction product of the present invention can be an aldehyde having 1 to about 6 carbon atoms. Formaldehyde is preferred and can be used in one of its reagent forms such as paraformaldehyde and formalin.

The polyamine used to prepare the Mannich reaction product of the present invention contains at least two or more amine nitrogen atoms and has at least one reactive N-H group capable of undergoing the Mannich reaction. The polyamine includes alkylenediamines, polyalkylenepolyamines, polyamines containing hydroxy groups and cyclic polyamines. The Mannich reaction product can be derived from the group consisting of ethylenediamine, propylenediamine, N,N-dimethylethylenediamine, N,N'-dimethylethylenediamine, N,N,N'-trimethylethylenediamine, N,N-dimethylpropylenediamine, N,N'-dimethylpropylenediamine, diethylene-

triamine, triethylenetetramine, 2-(2-aminoethylamino)ethanol, 4-(3-aminopropyl)-morpholine, and mixtures thereof.

5 The Mannich reaction product of the present invention can be prepared by reacting the alkyl-substituted hydroxyaromatic compound, aldehyde and polyamine by well known methods including the method described in U.S. Patent 5,876,468.

10 The fluidizer of the present invention comprises a polyether, a polyetheramine, or mixtures thereof. The polyether of the present invention can be represented by the formula $RO[CH_2CH(R^1)O]_xH$ where R is a hydrocarbyl group; R^1 is selected from the group consisting of hydrogen, alkyl groups of 1 to about 14 carbon atoms, and mixtures thereof; and x is a number from 2 to about 50. The hydrocarbyl group R is a univalent hydrocarbon group as described above for the hydrocarbyl-substituted polyamine, has one or more carbon atoms, and includes alkyl and alkylphenyl groups having about 7 to 30 total carbon atoms, preferably about 9 to 25 total carbon atoms, and more preferably about 11 to 20 total carbon atoms. The repeating oxyalkylene units are preferably derived from ethylene oxide, propylene oxide, and butylene oxide. The number of oxyalkylene units x is preferably about 10 to 35, and more preferably about 18 to 27. The polyether of the present invention can be prepared by various well known methods including condensing one mole of an alcohol or alkylphenol with two or more moles of an alkylene oxide, mixture of alkylene oxides, or with several alkylene oxides in sequential fashion usually in the presence of a base catalyst. U.S. Patent 5,094,667 provides reaction conditions for preparing a polyether. Suitable polyethers are commercially available from Dow Chemicals, Huntsman, ICI and include the Actaclear[®] series from Bayer.

25 The polyetheramine of the present invention can be represented by the formula $R[OCH_2CH(R^1)]_nA$ where R is a hydrocarbyl group as described above for polyethers; R^1 is selected from the group consisting of hydrogen, alkyl groups of 1 to 14 carbon atoms, and mixtures thereof; n is a number from 2 to about 50; and A is selected from the group consisting of $-OCH_2CH_2CH_2NR^2R^2$ and $-NR^3R^3$ where each R^2 is independently hydrogen or a hydrocarbyl group of one or more carbon atoms, and each R^3 is independently hydrogen, a hydrocarbyl group of one or more carbon atoms, or $-[R^4N(R^5)]_pR^6$ where R^4 is C_2 - C_{10} alkylene, R^5 and R^6 are

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independently hydrogen or a hydrocarbyl group of one or more carbon atoms, and p is a number from 1 to about 7. The polyetheramine is preferably derived from ethylene oxide, propylene oxide, or butylene oxide. The number of oxyalkylene units n in the polyetheramine is preferably about 10 to 35, and more preferably about 18 to 27. The polyetheramine of the present invention can be prepared by various well know methods. A polyether derived from an alcohol or alkylphenol as described above can be condensed with ammonia, an amine or a polyamine in a reductive amination to form a polyetheramine as described in European Publication No. EP 310875. Alternatively, the polyether can be condensed with acrylonitrile and the nitrile intermediate hydrogenated to form a polyetheramine as described in U.S. Patent 5,094,667. Polyetheramines where A is $-OCH_2CH_2CH_2NH_2$ are preferred. Polyetheramines are commercially available in the Techron[®] series from Chevron and in the Jeffamine[®] series from Huntsman.

The fuel composition of the present invention includes a combination of nitrogen-containing detergents comprising a hydrocarbyl-substituted polyamine and a Mannich reaction product as described above which can be in a weight ratio of the polyamine to the Mannich reaction product of about 0.2:1 to 1:0.2 and in other embodiments of about 0.5:1 to 1:0.5, of about 0.75:1 to 1:0.75, and of about 1:1. Each of the nitrogen-containing detergents can be present in the fuel composition at about 20-100 ppm by weight, preferably at about 22-80 ppm by weight, and more preferably at about 24-60 ppm by weight. The fuel composition optionally includes a fluidizer comprising a polyether, a polyetheramine, or mixtures thereof as described above where the weight ratio of the fluidizer to the combination of the nitrogen-containing detergents is less than 0.5, in another embodiment less than 0.3, and in a further embodiment less than 0.2.

In another embodiment of the present invention the fuel composition comprises the combination of nitrogen-containing detergents, the hydrocarbyl-substituted polyamine and Mannich reaction product, at or greater than about 60 ppm by weight as illustrated in the examples of Table 1 and 2 hereinbelow.

A method of the present invention of operating an internal combustion engine comprises fueling the engine with the fuel composition of the present invention which comprises the hydrocarbon fuel, the combination of nitrogen-

containing detergents, and optionally the fluidizer as described in this application. In another embodiment of the present invention, a method of controlling deposits in an internal combustion engine comprises fueling the engine with the fuel composition of the present invention as described in this application. The benefits
5 of the methods of the present invention are illustrated in the examples of Table 1 and 2 hereinbelow.

The fuel composition of the present invention can include a solvent to facilitate handling and transfer of fuel additives and fuel additive concentrates and to provide homogeneous fuel additive concentrates and fuel compositions. The solvent
10 can be an aliphatic hydrocarbon, aromatic hydrocarbon, glycol ether, alcohol, or mixtures thereof. Examples of suitable solvents include various naphthas, various kerosenes, benzene, toluene, xylenes, aliphatic alcohols having 2 to 10 carbon atoms, or mixtures thereof.

The fuel composition of the present invention can include additional fuel
15 additives depending on the requirements of the engine it is used in. In general the fuel composition can include antioxidants such as hindered phenols, supplemental detergents like succinimides, corrosion inhibitors such as alkenylsuccinic acids, antistatic agents, biocides, demulsifiers, and additional fluidizers such as mineral oils and poly(alpha-olefins). Gasoline fuel compositions can contain antiknock
20 additives such as methylcyclopentadienyl manganese tricarbonyl, haloalkane lead scavengers, and anti-valve seat recession additives such as alkali metal sulphosuccinate salts. Diesel fuel compositions can contain organo nitrite or nitrate cetane improvers, cold flow improvers such as copolymers of ethylene and vinyl acetate, smoke suppressants, antifoam agents like silicone fluids, and lubricity
25 agents such as tall oil fatty acids.

The fuel composition of the present invention is generally prepared by mixing the components which can include the hydrocarbon fuel, the nitrogen-containing detergents, fluidizer, solvent, and additional fuel additives at ambient temperature or at an elevated temperature of about 40 to 60°C until the mixture is
30 homogeneous. The various fuel additive and solvent components can be added to the hydrocarbon fuel separately but are usually added as a mixture or fuel additive concentrate which is prepared in the same way as the fuel composition.

Table 1BMW^a 2,500 Miles with Unleaded Gasoline Containing Ethanol

Example	A Hydrocarbyl Polyamine ^b , ppm actives	B Mannich ^c , ppm actives	Fluidizer, Ppm actives	Ratio of Fluidizer to A + B	Intake Valve Deposits, mg
1 (comparative)	61.6	—	31.6 ^d	0.51	282
2 (comparative)	68.4	—	35.1 ^d	0.51	85
3 (comparative)	30.2	—	46.4 ^e	1.54	172
4	31.7	32.7	3.9 ^e	0.06	48
5	36.0	37.1	—	—	43

Table 2BMW^a 2,500 Miles with Unleaded Gasoline

Example	A Hydrocarbyl Polyamine ^b , ppm actives	B Mannich ^c , ppm actives	Polyether ^d , ppm actives	Ratio of Polyether to A + B	Intake Valve Deposits, mg
6 (comparative)	68.4	—	35.1	0.51	25.4
7 (comparative)	—	57.5	28.3	0.49	23.0
8	40.0	41.2	—	—	8.6

^aFuel induction system deposit test run in BMW vehicle on intake valve deposits for 2,500 miles test cycle.

10 ^bHydrocarbyl-substituted polyamine from condensation of chlorinated 1300 molecular weight polyisobutylene and ethylenediamine.

^cMannich reaction product of a) alkylphenol from 1000 molecular weight high vinylidene polyisobutylene, b) formaldehyde and c) ethylenediamine.

^dPolyether from one mole of C₁₂₋₁₅ linear alcohol condensed with 22-24 moles of propylene oxide.

15 ^ePolyetheramine from one mole of C₁₂₋₁₅ linear alcohol condensed with 22-24 moles of propylene oxide, then cyanoethylation of the propoxylated alcohol with acrylonitrile and hydrogenation of the nitrile intermediate to form the polyetheramine.